

SUPPORTING INFORMATION

Spectroscopic and Redox Studies of Valence-Delocalized $[\text{Fe}_2\text{S}_2]^+$ Centers in Thioredoxin-Like Ferredoxins

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Figure S1: UV-visible absorption spectra of oxidized and dithionite-reduced WT *AaeFd4* at pH 7.0 and 11.0.

Figure S2: Film voltammograms of C56S *CpFd* at pH 7.2 and 9.8

Figure S3: Film voltammetry oxidative and reductive half-height peak widths (δ) for of C56S *CpFd* at pH 7.2 and 9.8 as a function of scan rate.

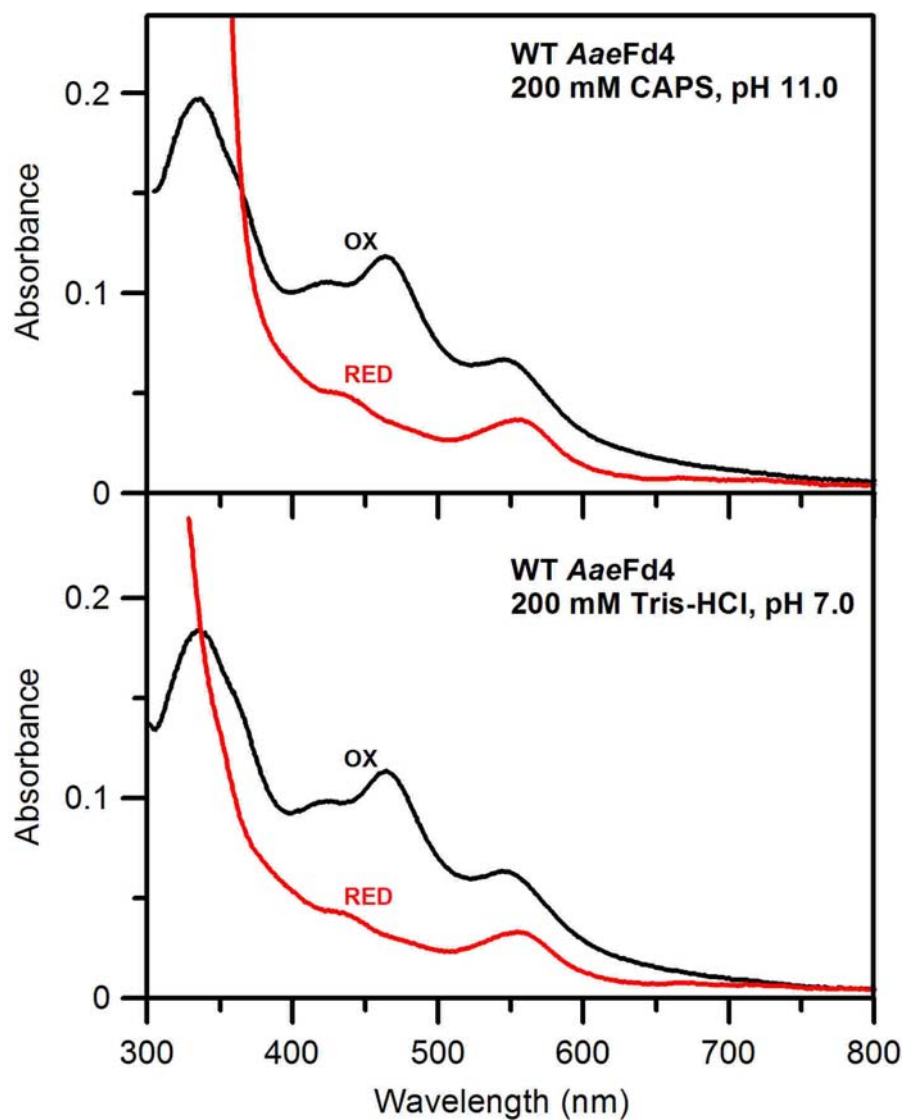
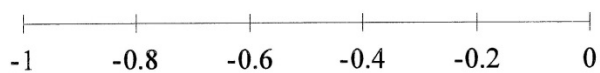
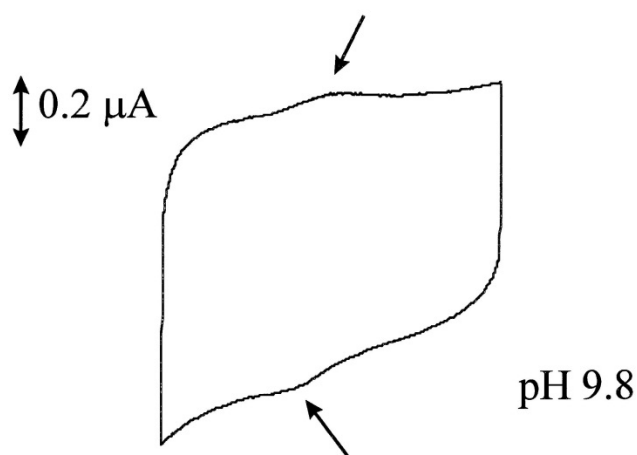
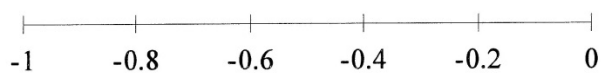
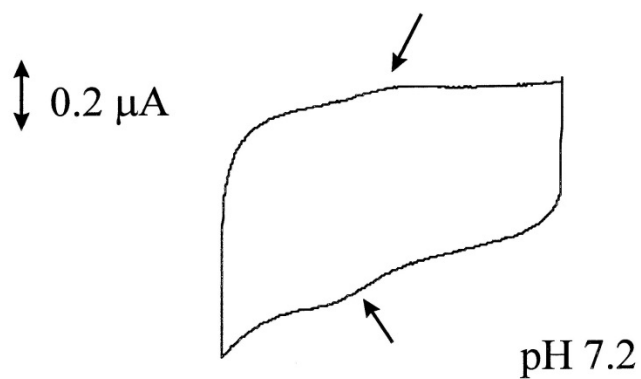


Figure S1. UV-visible absorption spectra of oxidized and dithionite-reduced WT *AaeFd4* (0.12 mM) in 200 mM CAPS buffer with 0.1 M NaCl at pH 11.0, and in 200 mM Tris-HCl buffer with 0.1 M NaCl at pH 7.0, recorded in 0.1 cm cuvettes.



E/V SHE

Figure S2. Film voltammograms of C56S CpFd at pH 7.2 and 9.8. Protein concentration ~0.1 mM in 20 mM mixed buffer (pH range 6.5-10.5) with 0.1 M NaCl and 200 μg mL⁻¹ polymyxin as coadsorbate. Voltammograms were recorded with a scan rate of 10 mV s⁻¹ at 0 °C. Very similar voltammograms were observed for C60S CpFd under analogous conditions.

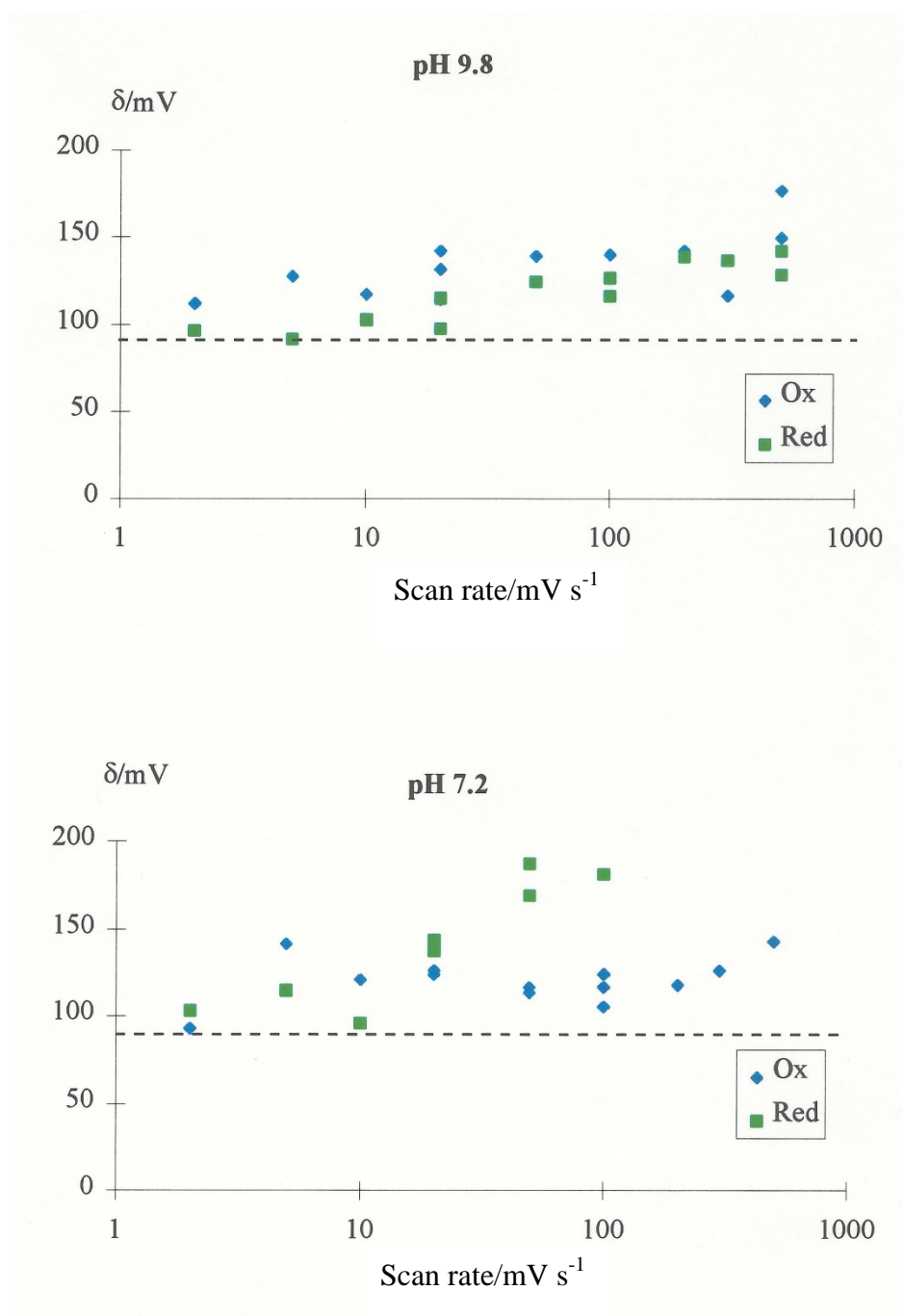


Figure S3: Film voltammetry oxidative and reductive half-height peak widths (δ) for of C56S CpFd at pH 7.2 and 9.8 as a function of scan rate. Conditions are the same as described in Figure S2. The dashed line indicates the ideal value of $\delta = 84$ mV. The reductive wave peaks were too broad to observe with scan rates > 100 mV s⁻¹ at pH = 7.2. The broader and more asymmetrical voltammetric waves that are observed at pH 7.2 are tentatively attributed to coupling to a ligand exchange reaction. Very similar results were observed for C60S CpFd under analogous conditions.